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SURFACE ENHANCEMENT OF SILICON CARBIDE FILAMENT FOR METAL MATRI--ETC(U)
JAN 81 R J SUPLINSKAS, H DEBOLT N00014-79-C-0691
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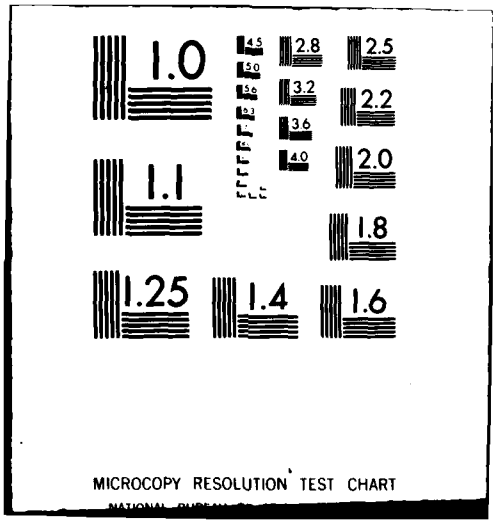
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SURFACE ENHANCEMENT OF SILICON CARBIDE FILAMENT

FOR

METAL MATRIX COMPOSITES

ONR CONTRACT N00014-79-C-0691

DTIC A

Summary Report

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Prepared For

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Office of Naval Research
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INTRODUCTION

The first year's efforts on this program were aimed at understanding the mechanisms of strengthening and degradation of SiC filament. Filaments were provided for analysis here in part by Avco IRAD and other related programs listed at the end of this report.

The specific objectives were:

1. Devise a model for filament strengthening/degradation effects due to the presence of surface layers or coatings on a brittle ceramic filament;
2. Determine properties of the carbon rich layer and propose mechanisms for filament strengthening;
3. Utilizing the above model and mechanisms, analyze alternative surfaces that can potentially:
   a. Provide surface strengthening
   b. Resist strength degradation in molten Al
   c. Bond with Al alloys during casting, hot molding or diffusion bonding operations.

Based on filament analysis conducted in this program by x-ray diffraction and SEM and Auger analysis the following observations are offered:

1. SiC is a crystalline material with grain boundaries normal to the substrate and stress axis.
2. Unrestrained grain boundaries, cleavage planes, or growth related defects in crystalline SiC open at low strains ($\sim$ 0.005 in/in which corresponds to a filament strength of 300 ksi) and propagate catistrophically.
3. The graded carbon-rich layer, when present effectively doubles the filament strength. This layer varies in composition from pure carbon at the surface to stoichiometric SiC at a depth of $\sim$0.5 μm. SEM fractographs show this layer to be hard, fire grained (or amorphous) and tightly adherent.
4. Auger analysis has shown that silicon in the C-rich layer is always bound as SiC. Excess carbon is present as free or elemental carbon.
5. The carbon rich surface bonds with difficulty to the common matrix alloys; e.g., Al or epoxy.
6. When bonding is effected by addition of reactive elements, it is accomplished by reaction with the filament surface. This reaction causes a recession of the filament surface. As little as 2000 Å surface recession causes a degradation in filament strength to uncoated values.

The conclusion of these observations becomes the basis of our new working hypothesis:

1. The fine grained carbon-rich layer seals the grain boundaries or other stress intensifying defects and prevents crack formation until stresses on the order of 1×10^6 psi are experienced by the filament.

2. The amorphous nature of the surface layer prevents new grain boundary cracks from being introduced into the surface.

3. The carbon rich surface must be altered to simultaneously provide bonding and seal defects.

The approach to the problem last year was as follows:

1. Evaluate methods for depositing fine grained or amorphous SiC on the SiC filament. The purpose being to duplicate the healing mechanism while providing a more bondable surface (for Al).

2. Altering existing surface to improve Al bondability/wettability of the filament surface by:

   a. Increasing Si/C ratio on the filament surface

   b. Overcoating the existing filament with B_4C, TiC, or TiN

3. Evaluate all filament modifications with SEM, EDX, x-rd grain size measurements and Auger analysis.

PROGRAM ANALYTICAL RESULTS

1. Deposition of fine grained stoichiometric SiC did not lead to improved filament properties. Indeed, the filament strengths were generally lower with the "ASiC" or amorphous SiC coatings than "standard" SiC with a C-rich surface.

2. Overcoating "standard" SiC with a thin ($\sim$ .2 μm) layer of amorphous B_4C permitted high strength castings to be produced (50 v/o, σ > 210 ksi) as long as exposure to molten aluminum was less than $\sim$ 2 min. Heavier coatings of B_4C resulted in as-produced filament degradation. This approach was abandoned on the standard SiC substrate.

3. Overcoating standard SiC with TiC and TiN r[illegible] in tolerance to molten Al and subsequent high cast rod data (+ 200 ksi t[illegible] 50 v/o composites). The production rates for coated filaments were considered too low to be economically feasible at this state of development. This approach was discontinued, but not abandoned.

4. Work continued in evaluating a controlled gradient modification of standard SiC. The silicon content of the surface was increased to improve bondability with Al (and epoxy) matrices. The many modifications of this filament are called "SCS". This filament or modifications of this filament have shown resistance to molten Al for times to 15 minutes at 1400°F and in excess of

1 hour at 1250°F. Composites have been fabricated by casting, hot molding, and diffusion bonding and were evaluated. The data are shown below in Tables Tables 1, 2, and 3 for diffusion bonded, hot molded and vacuum infiltrated composites,respectively.

5. Various modifications of this filament including BCS (B_4C coated SCS) have been composited with Ti 6 Al-4V in a companion AFML Program (Contract F33615-79-C-5012, Avco subcontract to Rockwell). These data are given in Table 4.

DISCUSSION OF RESULTS

A schematic representation of the composition profile of the surface treatment layer of the SCS filament is shown in figure 1. The Si/C gradient is reversed near the surface to provide a better surface for bonding to Al or resin matrices. The Si/C ratio drops to a rather low silicon level for better than half the coating thickness of the filament before the Si/C ratio again increases to stochiometric SiC at a depth of 0.4 to 2 μm depending upon the filament modification. In essence, the SCS surface treatment is composed of three zones:

a. The outer surface enriched in silicon, though still carbon rich, provides the bonding surface. (Zone I)

b. The inner zone consists of the normal gradient from stoichiometric SiC to an amorphous or fine grained carbon rich mixture of free carbon and SiC. This zone is responsible for healing defects and preventing low strain stress intensification at the transversely oriented columnar grain boundaries near their surface terminus. (Zone III)

c. The intermediate zone is carbon rich and provides the "forgivability" of the filament. This zone is a buffer that prevents surface reactions or cracks from inter-reacting with the sensitive inner gradient zone. (Zone II)

A glance at the transverse data of Tables 1, 2, and 3 point out a weakness in the present modification of the SCS filament. The aerospace industry has taken the B/Al as their standard of excellence. B/Al (6061) typically has a transverse strength of the order of 20 ksi in the as diffusion bonded condition. The typical transverse strength of SCS/Al 6061 composites are of the order of 10 ksi although they can be T-6 heat treated to ∿ 15 ksi. The reason for the low transverse strength values becomes obvious when one views the composition profile and SEM photographs of composite fracture surfaces. Figure 2 shows an axial tensile specimen fracture surface. The crazed surface layer is strongly adherent to the matrix. The layer is delaminated from the filament surface during failure. Figure 3 shows a transverse fracture surface of the same panel. Shown here is the entire outer layer adherent to the matrix while the filaments are either split or pulled away with the inner layer. The higher magnification photograph of the filament pull-out region and EDX scan of figure 4a shows the inner gradient layer tightly adherent to the SiC filament chip. Thus, we must conclude that the carbon rich "valley" is weak and is the source of the low transverse properties.

TABLE 1
DIFFUSION BONDED SCS/AL 6061
1080°F/30 MINUTES/5 KSI
(46 v/o)

SAMPLE #	σ_{II} KSI	ϵ_{II} %	E_{II} MSI	σ_{22} KSI	E_{22} MSI
1 (80-467)	290	1.11	31.2	11.3	18.2
2	258	1.05	29.4	8.2	18.5
3	227	.91	29.1	10.3	19.7
4				10.5	20.5
1 (80-252)	257	1.13	33.4	8.3	15.5
2	223	1.10	31.1	10.1	19.4
3	218	1.16	30.5	9.2	20.3
4	229	1.12	32.2		

TABLE 2
HOT MOLDED SCS/ALUMINUM
SCS IN 6061/713 BI-ALLOY MATRIX
1110-1120°F/20 MINUTES/800 PSI
(48 v/o)

SPECIMEN NO.	σ_{11} KSI	ϵ_{11} %	E_{11} MSI	σ_{22} KSI	E_{22} MSI
80-466A-1	245	1.0	31.2	9.1	17.5
-2	272	1.04	31.0	10.0	21.6
-3	272	1.03	29.8	11.4	21.0
-4	270	1.06	29.5	11.8	20.6
-5	254	1.0	28.4	9.6	21.6

TABLE 3
SCS/AL CAST RODS
(A357 AT 1250°F)

SAMPLE #	EXPOSURE TIME/MIN	UTS (KSI)	ϵ STRAIN TO FAILURE %	E MODULUS (MSI)	V/O FIBER VOL FRACT %
80-3/14-5 +	1	233	0.72	34.5	50
-4	5	253	0.76	33.6	50
-6	15	246	0.81	31.5	50
-7	5	207	0.75	29.2	38
80-11/10-1 ++	5	247	0.82	35.1	52
-2	5	+266*	0.84*	35.0	52
-4	5	+228*	0.74*	33.9	52

* SPECIMENS PULLED OUT OF GRIP AND DID NOT FAIL, VALUES GIVEN ARE MEASUREMENTS AT TIME OF SLIPPAGE.

\+ FIBER LOT 35-338
++ FIBER LOT 82880, 83450, 79750

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TABLE 4 - PAGE 1

TENSILE DATA FOR VARIOUS MODIFICATIONS
OF
SCS FILAMENT IN A TI-6AL-4V MATRIX*

SPECIMEN #	$\sigma 0°$ KSI	$\epsilon 0°\%$	$E0° \times 10^{-6}$ PSI	$\sigma 90°$ KSI	$\epsilon 90°\%$	$E90° \times 10^{-6}$ PSI
SCS-2/TI 6-4						
80-587-1	136.9	0.46	30.8	60.0	0.40	25.2
-2	142.1	.46	31.2	57.5	.35	23.2
-3	144.2	.47	31.3			
-4	150.6	.51	30.0			
$\bar{\sigma}$ =	143.5					
BCS/TI 6-4 **						
80-591-1	168.1	0.56	30.1	52.9	0.28	25.6
-2	174.4	0.60	29.4	54.0	0.33	21.0
-3	170.7	0.58	29.7	56.6	0.36	21.6
-4	174.7	0.59	30.1			
-5	168.0	0.56	30.4			
-6	167.1	0.57	29.3			
$\bar{\sigma}$ =	170.5					

* Consolidated ½ Hr At 1700°F, 6 ksi, All panels 35 v/o

** BCS is B_4C Coated SCS-2

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TABLE 4 - PAGE 2
TENSILE DATA FOR VARIOUS MODIFICATIONS
OF
SCS FILAMENT IN A TI-6AL-4V MATRIX

SPECIMEN #	$\sigma 0°$ KSI	$\epsilon 0°\%$	$E0° \times 10^{-6}$ PSI	$\sigma 90°$ KSI	$\epsilon 90°\%$	$E90° \times 10^{-6}$ PSI
SCS-5/TI 6-4 THICKNESS = 1.25 μM						
80-588-1	189.1	0.66	29.2	58.5	0.40	24.1
-2	182.3	0.64	28.6	58.6	.38	23.6
-3	184.4	0.61	30.0	58.1	0.40	24.7
-4	173.5	0.59	29.3			
-5	183.3	0.64	29.0			
-6	191.7	0.65	29.8			
$\bar{\sigma}$ =	184.5					
SCS-6/TI 6-4 THICKNESS = 2 μM						
80-589-1	242.1	0.95	28.9	58.5	0.36	25.1
-2	217.4	0.83	28.5	57.5	.35	23.6
-3	217.6	0.79	29.7			
-4	229.6	0.86	30.1			
$\bar{\sigma}$ =	226.7					

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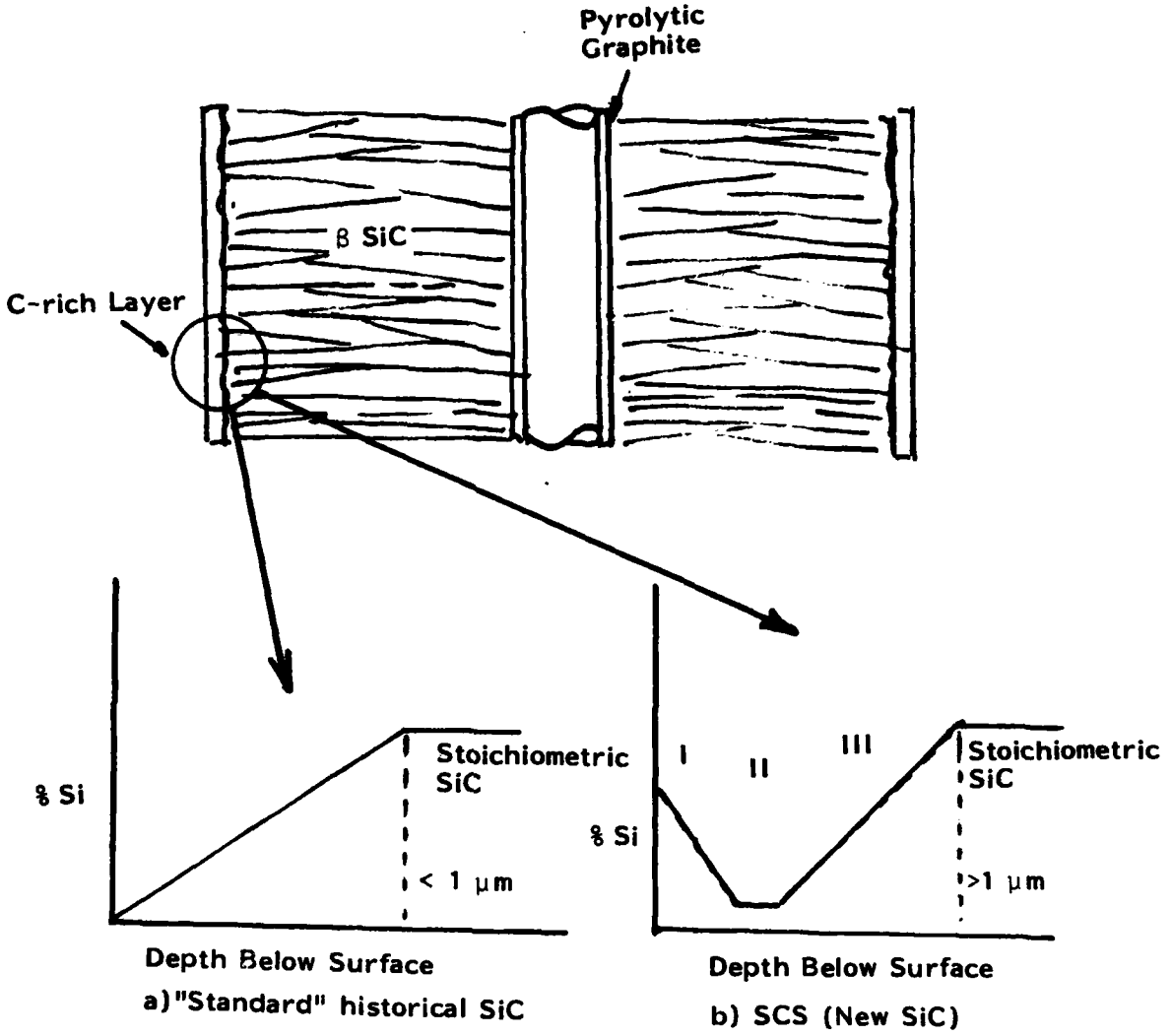

Figure 1 Schematic Representation of a Longitudinal Section Through a Silicon Carbide Filament Grown by CVD Techniques

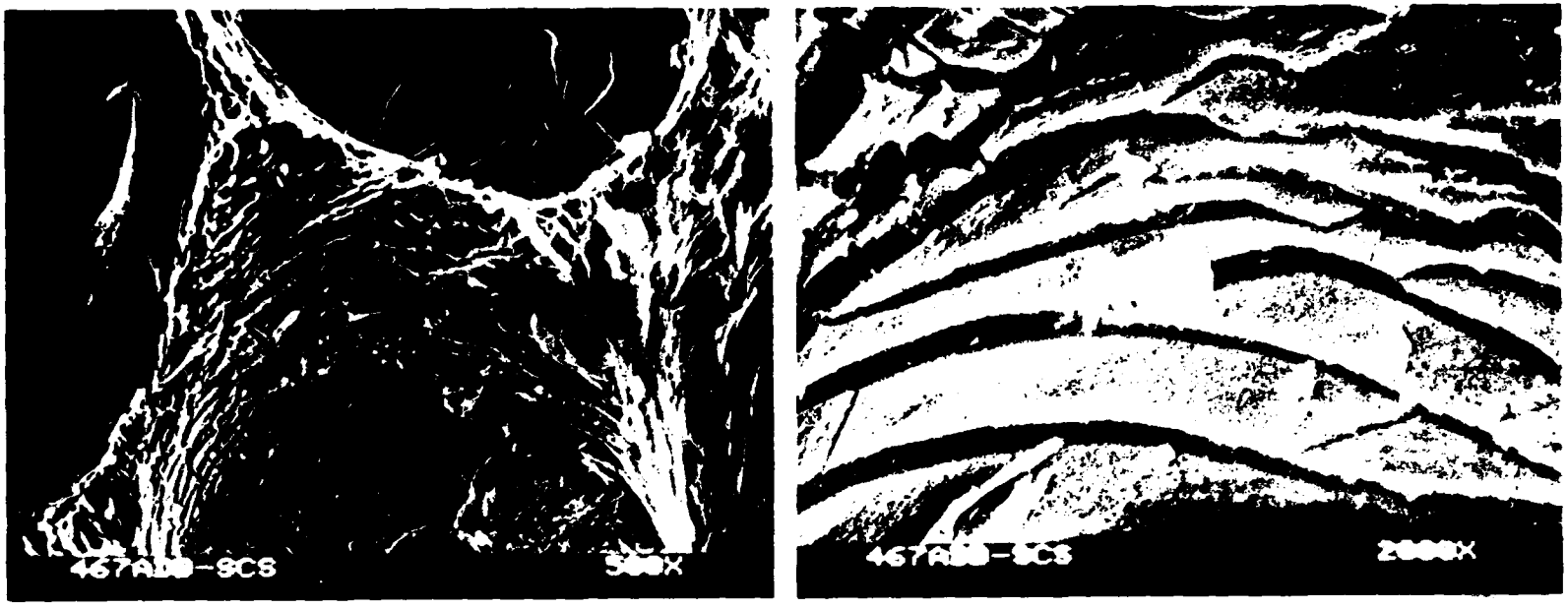

Figure 2 AXIAL FRACTURE FEATURES OF A SCS-2/6061 DIFFUSION BONDED SPECIMEN SHOWING CRAZING OF OUTER PORTION OF C-RICH LAYER

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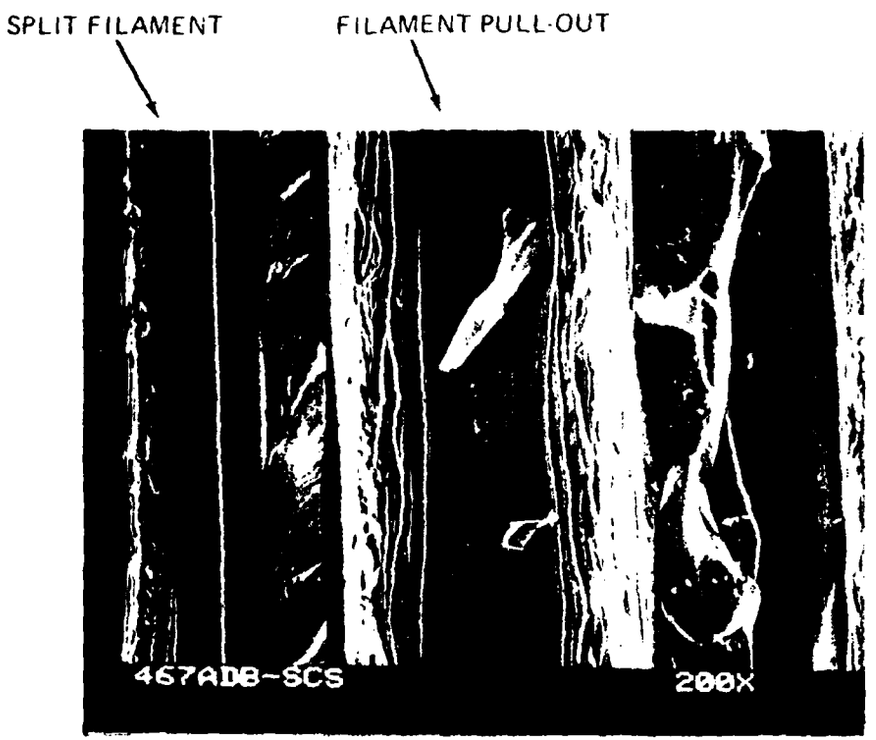

Figure 3 Transverse Fracture Features of SCS-2/6061 Composite Fabricated by Diffusion Bonding

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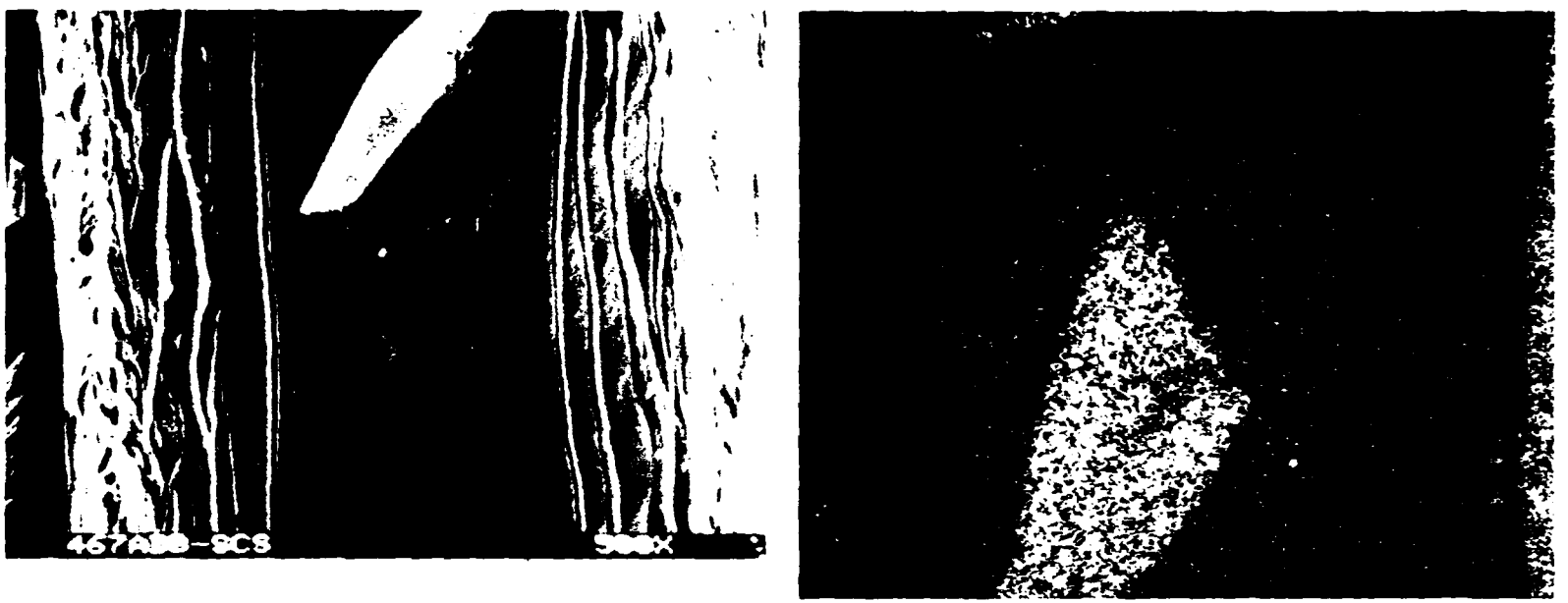
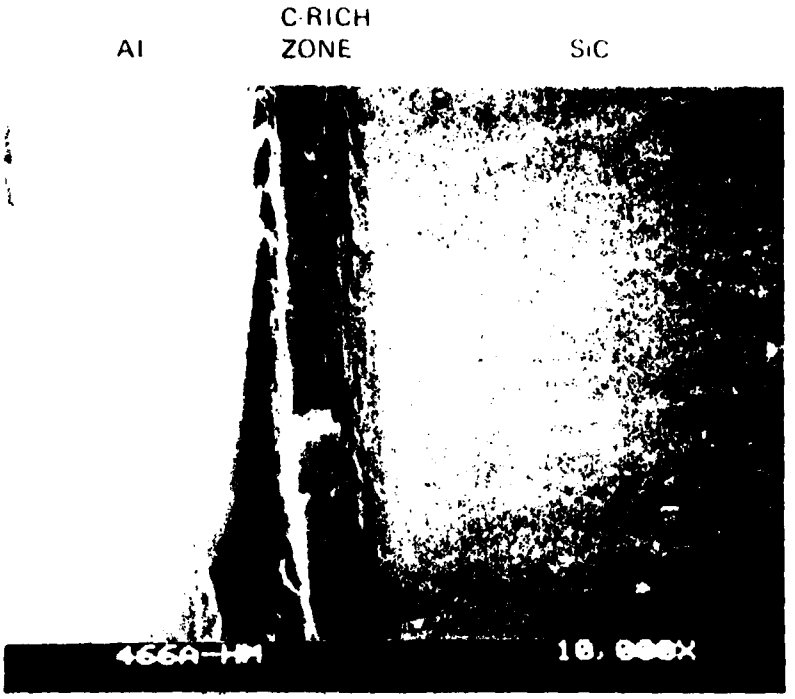


Figure 4 TRANSVERSE FRACTURE FEATURE OF SCS-2/6061 DIFFUSION BONDED SPECIMEN

a) Is a Cavity Showing Outer Portion of C-Rich Zone Adherent to Al.

b) Is a Si EDX Scan Showing a Chip of SiC Adherent to the C-Rich Zone.



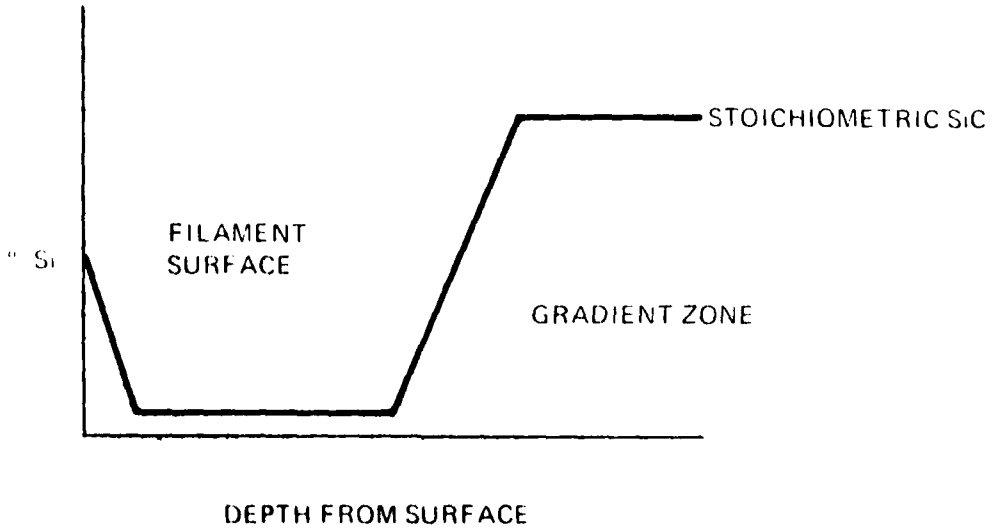


Figure 5 TRANSVERSE FRACTURE SURFACE SHOWING A SPLIT FILAMENT REVEALING THE C-RICH ZONE AND SCHEMATIC REPRESENTATION OF Si GRADIENT WITHIN ZONE

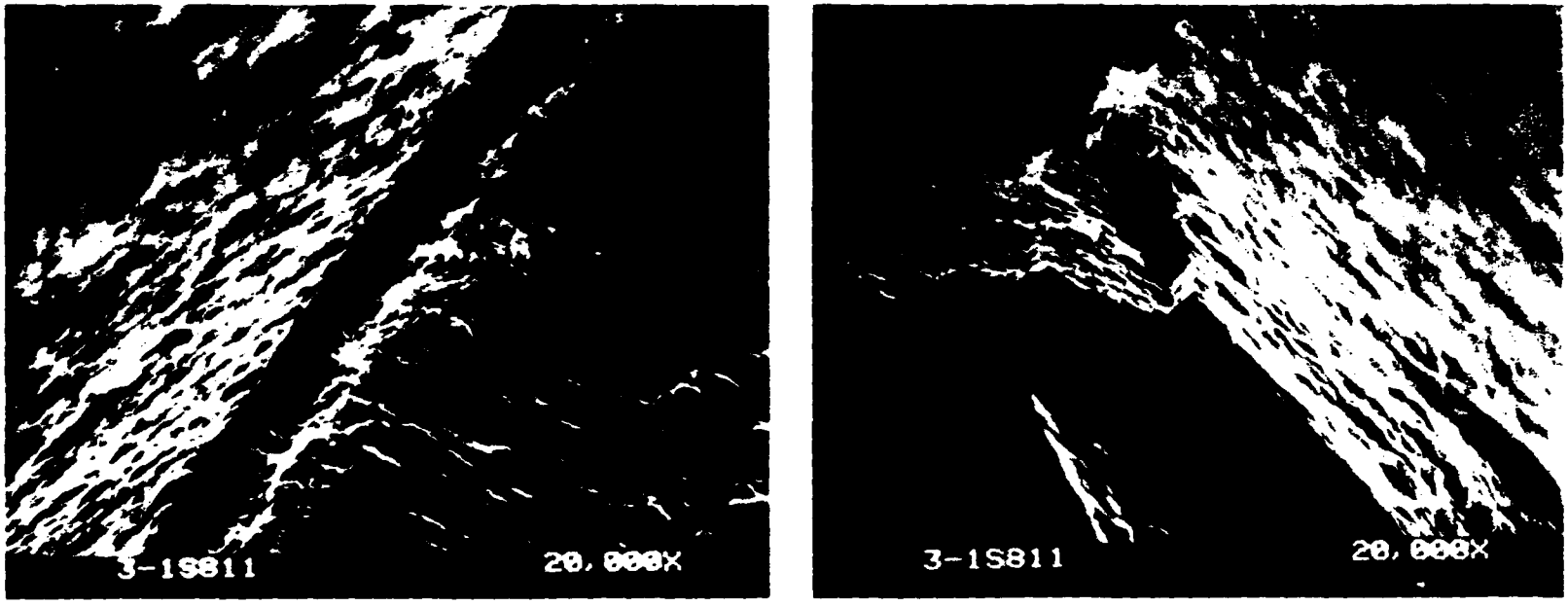


Figure 6 SURFACE STRUCTURE OF SCS 3

NOTE: CRYSTALLINE APPEARANCE
OF SURFACE LAYER

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Work was initiated to improve the transverse properties of the filament by strengthening the carbon rich layer. Various modifications of reactor design and parameters were investigated. The new "standard" SCS filament modification was given the designation SCS 2 and is shown in figure 5 with a schematic gradient. Various other modifications, SCS 3, SCS 5, and SCS 6 were investigated and SEM micrographs of a fracture cross section of the filament surface layers are shown in figures 6, 7, and 8, respectively. Auger composition profiles taken from reactor tails* are shown in figure 9 for SCS 2, 3, 5 and 6. Attempts were made during the deposition of SCS 3, 5 and 6 to increase the Si content of the surface layer without causing crystalline deposition of the surface layer. The SEM photographs of SCS 2 in figure 5 shows a faint layered surface. We may surmise that delamination can occur easily in this structure.

SCS 3 is deposited in a short reactor ($\sim$ 6" long vs $\sim$ 24" long for the modifications discussed here). Extra silicon was added to the surface to increase the inner zone strength. The fracture texture shown in figure 6 gives a crystalline appearance which corresponds to low axial properties. It is interesting to note that the transverse properties of SCS 3 were superior to the other modifications discussed here ($\sim$ 12-15 ksi) although the axial strengths were lower. The composition profile in figure 9 shows SCS 3 to have the highest Si content in the central regions of any of the filaments evaluated to date.

SCS 5 and 6 have not been investigated in Al matrices yet, although the SEM microstructure revealed in figures 7 and 8 show similar layering to SCS 2, which led to low transverse properties.

The composition profiles in figure 9 are worthy of more comment. The inner composition gradient which is responsible for the filament strength appears to be very steep. A more gentle gradient should eliminate the sharp delamination zone. In addition, a higher silicon content at the surface and in the intermediate zone should simultaneously improve the strength of the intermediate zone and improve the wettability of the filament to molten alloys.

FUTURE WORK

1. Continue variations of reactor design and deposition parameters to produce filament with higher transverse properties in Al alloy matrices.
2. Explore compositional limits for producing "glassy" carbon rich deposits.
3. Characterize interfacial reactions and surface recession phenomena of various SCS modifications in molten Al.
4. Evaluate longitudinal and transverse composite panel properties and relate to microstructure.
5. Evaluate selected modification of SCS filament in titanium matrix alloys.

* A reactor tail is obtained by simultaneously switching off filament heating current and filament take-up. The resulting tail freezes the deposition process. Auger surface analyses of an indexed location on the reactor tail will reveal the composition being deposited at that location in the reactor. Thus, composition profiles can be obtained without time consuming sputtering.

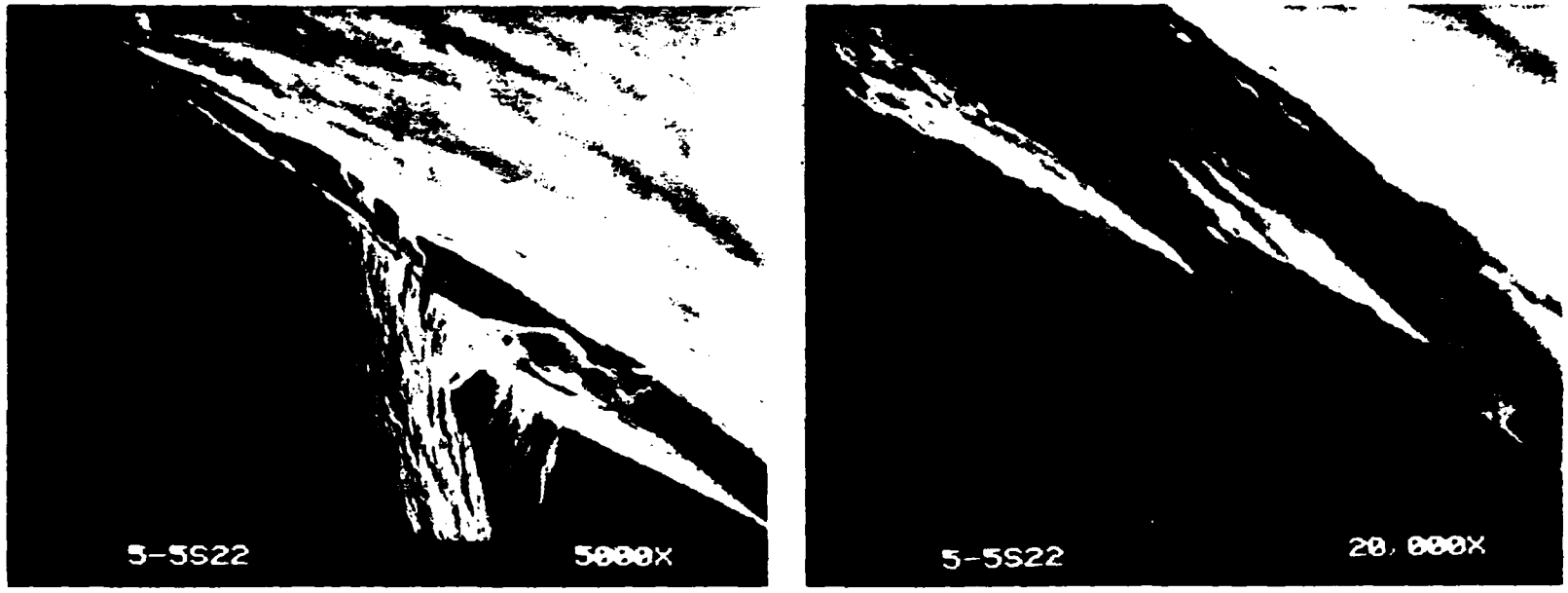

Figure 7 SURFACE COATING FOR SCS 5 AS-PRODUCED

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Figure 8 SURFACE STRUCTURE OF SCS 6

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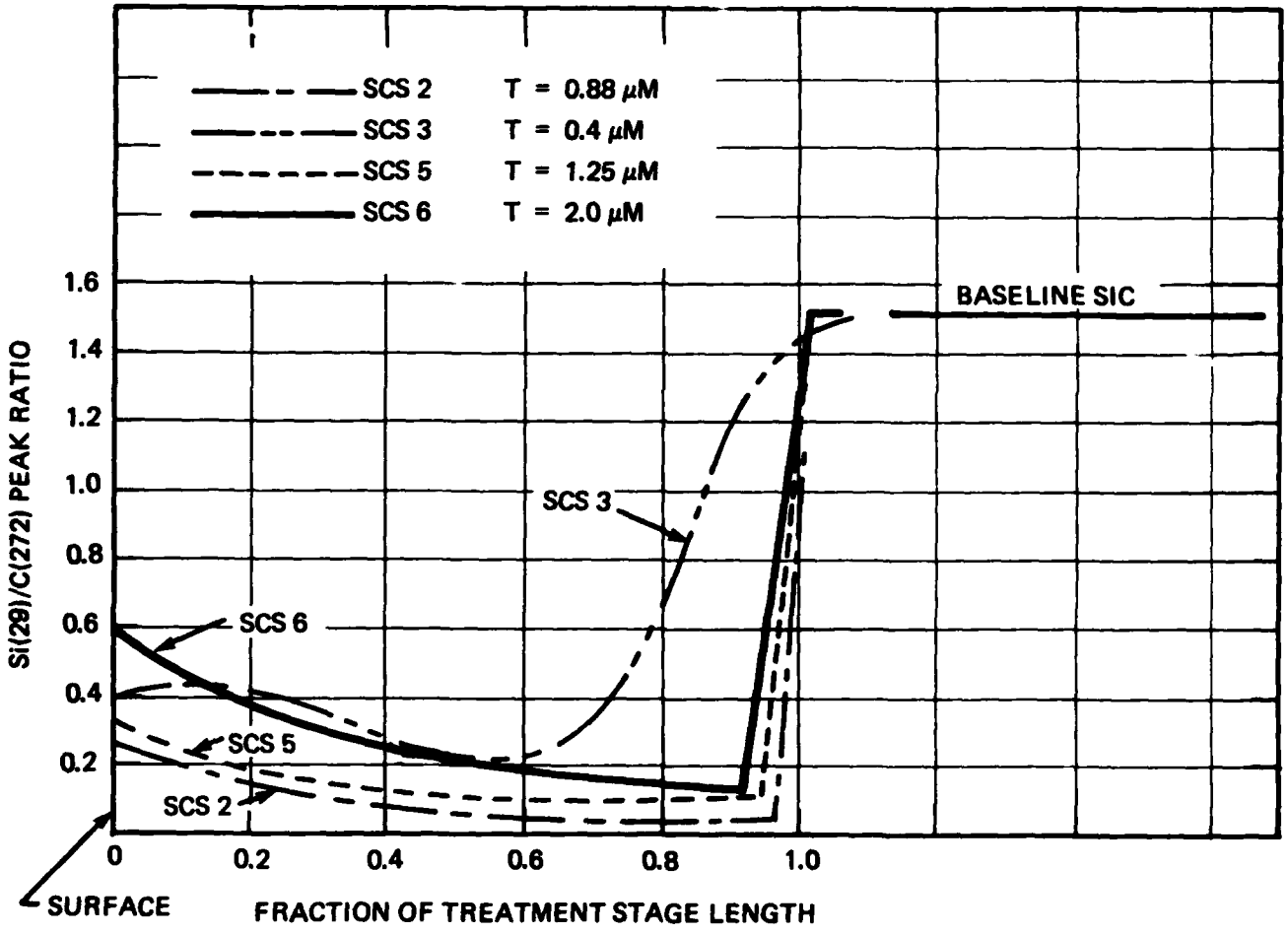

Figure 9 Auger Analysis of SCS Reactor Tails